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EFFECT OF IRON OXIDES ON THE PRONENESS OF SYNTHESIZED BASALTIC METALS TOWARD FIBER FORMATION

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The results of experimental studies of the physical-chemical parameters of basaltic glass synthesized by reduction melting of batch from dolerite and limestone and differing by the total content of bi- and trivalent iron are presented. It is shown that as the iron oxide content in the melt decreases the capability of the melt to form continuous fibers decreases because the structure of the glass breaks down and the fibers become weaker.

Key words: rocks, synthetic basalts, reduction melting, deferrized melts, glass, viscosity, crystallization and wetting powers, temperature interval of fiber production.

Rocks of magmatic origin serve as raw materials for the production of basaltic fibers. However, it should be noted that if most basaltoid rocks are suitable for obtaining staple fibers (mineral cotton), the list of such rocks that are suitable for forming continuous fibers possessing unique properties — high strength, heat, acid, alkali, and moisture resistance, and durability — is very short. For this reason the search for raw materials for producing continuous fibers is certainly a topical problem.

The statistical study of the chemical composition of basalts of different types has shown that they contain on average from 3 to 5% Fe_2O_3 and from 6 to 9% FeO. Ordinarily, fresh basalts unaltered by secondary processes contain much more FeO than Fe_2O_3. This is explained by rock formation at depths inside the Earth where a reducing medium at low oxygen partial pressure predominates. Volcanic melted basalt in air, where the oxygen partial pressure (0.2 atm) is much higher than deep inside the Earth, rapidly oxidizes, as a result of which the Fe_2O_3 content in the basalt increases and the FeO content decreases. The total content of the two oxides (Fe_xO_y) remains unchanged [1]. The process of oxidation of basaltic melt changes the physical-chemical properties of the melt. Since Fe_2O_3 in silicate melts serves as a network former while FeO is a modifying agent, an increase of the trivalent iron content with a decrease of ferrous oxide increases the viscosity of the melt, which is the main criterion for the production properties of the melt.

As a result of oxidation, depending on the soaking time in air, the viscosity of the basalt in the melted state increases more strongly than even with a decrease of temperature. Hence, rocks with a low content of iron oxides are preferable for drawing continuous fiber. In addition, basaltic melts containing Fe^{2+} possess elevated wetting power and interact with platinum-rhodium alloys which are used to make the equipment needed to obtain continuous fiber. As a result, the spinneret field is "filled in," the temperature interval for fiber production becomes limited, and expensive equipment wears out more quickly. Since basaltic raw materials with low iron content do not occur everywhere in Russia, there is promise in using synthesized low-iron glasses for such purposes. On this basis, in the present work we investigated the possibility of using for the production of continuous fiber silicate melts synthesized in the process of reduction melting of batch containing dolerite and limestone in the ratio 80 : 20 by weight. Test samples with different Fe_xO_y concentration which were taken in definite reduction time intervals τ_{red} were delivered to Special Design and Technology Office "Nauka" at the Krasnoyarsk Science Center of the Siberian Branch of the Russian Academy of Sciences.

It is evident from the data presented in Table 1 that as the reduction melting time increases the content of iron oxides in the glass samples decreases, which causes a redistribution of the concentrations of other elements.

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TABLE 1. Chemical Composition of Synthesized Glasses

τ_{red}, h	Content of oxides, wt.%									
	SiO_2	Al_2O_3	Fe_xO_y	CaO	MgO	SO_3	Na_2O	K_2O	Cr_2O_3	TiO_2
0	43.02	13.35	9.73	22.78	7.40	0.20	2.30	0.75	0.30	0.15
74	44.14	15.53	4.91	24.61	6.10	0.17	2.99	0.64	0.64	0.10
122	43.58	16.19	2.40	24.64	8.00	0.17	2.85	0.56	0.62	0.10
140	45.20	15.92	2.10	24.26	7.95	0.22	2.85	0.86	0.62	0.15
200	44.65	14.72	0.30	29.02	6.30	0.35	1.55	0.54	0.35	–

The acidity modulus M_a was calculated from the ratio of the basic and acidic oxides:

$$M_a = \frac{SiO_2 + Al_2O_3}{CaO + MgO},$$

where SiO_2, Al_2O_3, CaO, and MgO represent the content of the oxides by weight, %.

For the synthesized compositions M_a lies in the range 1.68 – 1.94, which is much lower than the values of this parameter recommended for basaltic glass used for the production of continuous fibers.

The proneness of a mineral raw material to form continuous fiber is determined by the working interval of the viscosity (temperature) of the melt, whose upper limit is bounded by the temperature at which the melt spreads over the spinneret plate of the feeder, while the lower limit is bounded by the temperature at which crystals form in the glass.

A RVTs-K90R4 digital rotary viscosimeter was used to measure the viscosity at temperatures from 1450 to 1200°C (every 50°C) after the melt is has undergone isothermal soaking for 30 min at each given temperature to establish equilibrium. The arithmetic-mean of the viscosity calculated from three indications on the electronic indicator board of the viscosimeter were taken as the final result.

The criterion of the degree of wetting of a solid by the melts is the contact angle. The most widely used method of determining the contact angle essentially reduces to scanning a drop of molten glass cooled together with the platinum, ceramic, or other plate in a projection apparatus [2]. The limiting contact angle of the platinum-rhodium alloy for the experimental melts was measured at temperatures from 1200 to 1350°C according to the following scheme. A special device was used to form glass powder into tablets and place the tablets onto platinum-rhodium foil in a furnace preheated to a prescribed temperature at which the tablets were held for 30 min. After cooling, the samples were placed into the projection apparatus, where the limiting contact angle was measured with a protractor at four points along the circumference on the projection of a drop.

The crystallization power was evaluated by the method of forced crystallization [3], which is distinguished by its simplicity and permits obtaining the required results quite rapidly. For this, powder consisting of the experimental glass was placed into a platinum crystallizer boat in a horizontal gradient furnace preheated to 1400°C. The winding of the furnace chamber is arranged so that the maximum temperature is produced at the center of the furnace and the temperature gradually decreases toward the edges to the glass softening value. A thermocouple, which has feedback with the heater, is placed at the center of the furnace. The constancy of the temperature at the center of the furnace also creates constancy of the temperature gradient in it. The crystallizer with the glass powder was held in the furnace for 3 h, after which it was removed and rapidly cooled. The calibration curve was used to find the temperature of the upper limit of crystallization, characterizing the lower limit of the temperature interval of fiber production.

The temperature interval for fiber production was determined on a one-spinneret laboratory setup which included a vertical electric furnace with platinum-rhodium heater and an alundum ceramic chamber with an opening cut in the bottom, a winding facility with a regulated rate of rotation of the drum, and a platinum crucible with a 3.6 mm in diameter spinneret. In the experiment the lower temperature of the fiber production interval at which the melt freely flows through the spinneret and the fiber can be directed onto the drum of the winding facility was held fixed and the upper temperature at which the melt starts to spread over the spinneret field was changed in steps of 10 – 15°C. Previous experiments showed that the temperature of the melt in the furnace differs from that at the exit from the spinneret by 120 – 150°C, but since definite difficulties are encountered in practice when measuring the latter, data on the temperature recorded in the furnace chamber were used for comparative evaluation of the temperature interval of fiber production. The winding speed was 1830 m/min.

A BIOLAM-I microscope with 1000-fold magnification was used to measure the fiber diameter d.

A scales-type dynamometer was used to measure the tensile strength σ_t of the elementary continuous fibers. The arithmetic-mean of 20 tests was taken as the true value. The strength was calculated using the relation

$$\sigma_t = 4P/\pi d^2,$$

where P is the rupture load, in N, and d is the diameter of an elementary fiber, in m.

TABLE 2. Physical-Chemical Parameters of Glasses

Parameter	Parameter value					
	Glass with Fe_xO_y content, wt.%					Basaltic glass
	0.30	2.10	2.40	4.91	9.73	
Viscosity, Pa · sec, at temperature, °C:						
1450	1.87	1.72	1.70	1.52	1.24	7.8
1400	2.70	2.36	2.35	2.05	1.45	13.0
1350	4.14	3.62	3.54	3.24	2.10	23.0
1300	7.27	5.05	5.07	4.80	2.95	41.0
1250	12.82	9.82	9.60	7.75	4.93	77.0
1200	19.97	19.50	19.30	14.90	8.43	–
1150	28.00	27.80	26.20	24.80	13.20	–
Limiting contact angle, °, at temperature, °C:						
1200	83.0	86.5	86.0	83.0	85.5	86.5
1225	79.5	85.0	84.0	80.0	85.0	21.5
1250	61.5	35.0	32.5	28.0	22.5	18.0
1275	38.0	32.5	30.5	24.0	21.5	15.0
1300	36.0	30.5	29.5	20.5	21.0	13.0
1325	31.5	28.5	29.0	20.0	21.0	6.0
1350	–	–	–	–	–	*
Upper crystallization temperature, °C	1205	1210	1212	1210	1220	1270

* Wetting.

The principal physical–chemical properties of the synthesized glasses are compared in Table 2 with the characteristic parameters of most melts obtained from the natural raw material — basalts.

The low values of the acidity modulus (1.68 – 1.94) give low melt viscosity. It is evident from Table 2 that as the total content of iron oxides in the glass increases, the melt viscosity decreases in the entire experimental temperature range, and especially strongly at low temperatures.

In accordance with published data [1, 4] and the experimental data obtained by the present authors, continuous fibers are formed consistently from melts with viscosity 10 – 30 Pa · sec. For synthesized melted glasses this viscosity level is attained in the interval 1150 – 1250°C, which makes it possible to talk about lowering the temperature at which they are processed into fiber, and therefore about decreasing the energy consumption for this process.

Because the content of iron oxides is low the wetting power of the synthesized glass is low compared with basaltic glass: their complete spreading over a platinum-rhodium plate occurs at temperatures 50 – 75°C higher than in most rock melts. As a rule, low spreadability has a positive effect on the expansion of the temperature interval of fiber production, but in the case of the glasses studied here the upper temperature of this interval will be determined not by the limiting contact angle but rather by the working viscosity of the melt.

The suitability of the melt for the production of continuous fiber can be judged indirectly from the activation energy ΔE_η of viscous flow. As indicated in [5], the value of ΔE_η for melts from which continuous fibers are formed must not exceed 270 kJ/mole. Analysis of the energy parameters calculated from the slope of the curves presented in Fig. 1 showed that the values found for ΔE_η (from 180 t0 210 kJ/mole)

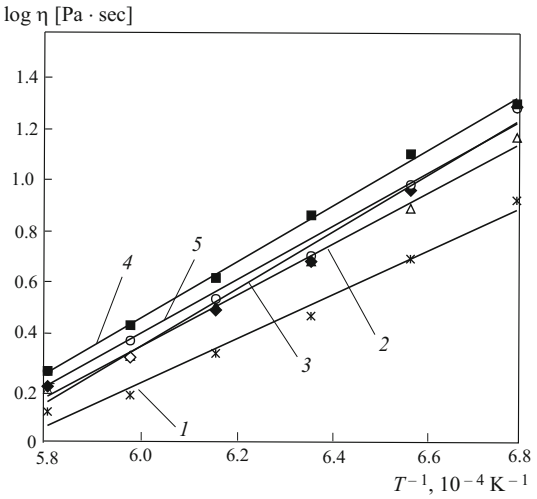

Fig. 1. Plots of the logarithm of the viscosity of melts with different Fe_xO_y content versus the reciprocal of the temperature: *1*) 9.73%; *2*) 4.91%; *3*) 2.40%; *4*) 2.10%; *5*) 0.30%.

TABLE 3. Strength Characteristics of Fibers

Fe_xO_y content, wt.%	Temperature, °C	Index values		
		d, μm	*P*, kN	σ_t, MPa
0.30	1300	21.3	20.6	580
2.10	1300	15.8	12.7	650
	1310	14.6	11.0	658
2.40	1300	15.3	12.6	685
	1310	14.6	12.0	720
4.91	1300	16.0	19.2	960
	1320	15.3	18.7	1020
	1330	15.0	18.5	1050
9.73	1300	13.4	18.8	1330
	1320	12.8	20.0	1550
	1330	12.6	21.1	1670
	1350	12.1	22.3	1960

make it possible to suppose that it is possible to produce continuous fibers from the experimental samples.

Another factor having a positive effect on the temperature of fiber production is the low upper limit temperature of crystallization of the experimental glasses.

Since fiber manufacture is, as a rule, a very energy intensive process, the low viscosity and low crystallization and wetting powers compared with natural-basalt melts make synthetic-basalt melts promising economically because manufacturing can be done at lower temperatures, thereby lowering production costs.

However, even though the production properties of the synthesized melts are quite good, their use in fiber manufacture gave rise to definite difficulties. Very small particles of metallic iron, which are formed during reduction melting of batch, settle on the bottom of the crucible during fiber formation and plug the spinneret openings, causing the fibers to break. In addition, when the glass is repeatedly heated to the melting temperature it undergoes repeated degassing, which likewise results in the appearance of internal and surface defects (Fig. 2) and, in consequence, breaks appear in the fiber.

The strength characteristics of elementary fibers obtained using synthesized glasses at different temperatures are presented in Table 3.

As the formation temperature increases, the fiber diameter decreases and the fiber strength increases. Aside from the effect of the scale factor (diameter) on fiber strength [6], there is a clear tendency for the fiber strength to decrease as the Fe_xO_y content in the melt decreases. Since trivalent iron

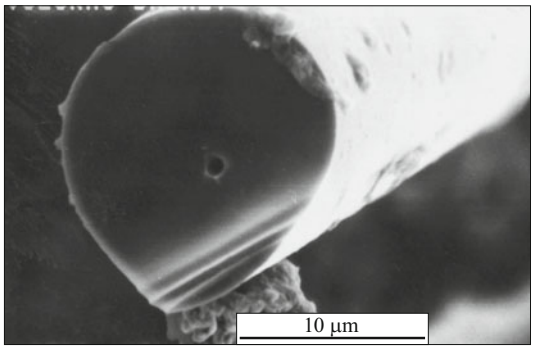

Fig. 2. Photomicrograph of an elementary fiber obtained from melt containing 2.40 wt.% Fe_xO_y.

cations can be incorporated into the structure of the glass, i.e., are network formers, we suppose that removing them from the glass will decrease fiber strength. The fiber structure becomes less dense, and weakened sections along which a break in formation occurs appear in it. Hence it follows that to obtain high-strength continuous fibers from deferrized melts the damaged structure of the glass must be repaired, which, apparently, can be done by introducing other network formers, for example, Al_2O_3.

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